Paper No.
05422
CORROSION 2005

# MICRO-ALLOYING IMPROVES RESISTANCE TO HIGH TEMPERATURE ENVIRONMENTS

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## ABSTRACT

Modern melting and refining techniques have given stainless and nickel alloy users the capability to control alloy content to precise narrow ranges. This ability in conjunction with market needs for heat resistant stainless steels that could offer properties competitive with more costly nickel alloys led to the development of alloys such as S30815 in the 1970s, and S35315 in the 1980s. More recently these techniques were also applied to develop N06025, as a means to enhance a nickel alloy so that it could offer improved properties versus traditional alloys such as alloy 600 and alloy 601. Microalloy additions of rare earth metals such as cerium and yttrium enhance scaling resistance and creep strength. Elevated levels of nitrogen and/or carbon enhance mechanical properties at elevated temperatures.

Results of laboratory oxidation testing and creep rupture property comparisons are provided along with several case histories.

Keywords: Alloy 353 MA®, 602CA®, 253 MA®, oxidation, sulfidation, UNS S35315, UNS S30815, UNS N06025, creep rupture.

## INTRODUCTION

Development work was started on alloy 253MA[1] (UNS S30815) at the former Avesta Stainless (Now Outokumpu Stainless) in 1971. The aim at that time was to create an alloy with at least the properties of the established heat resistant stainless steel 310S (UNS S31008), but with a lesser alloying content.

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(1) 253MA and 353MA are registered trademarks of Outokumpu Stainless

The chemistry of S30815 is compared to 310 stainless in Table 1. S30815, like 310 stainless, has a fully austenitic structure. Dramatic improvements in high temperature properties result from microalloying with cerium (oxidation, creep strength), silicon (oxidation), slightly higher carbon (creep strength), and significantly higher nitrogen (creep strength)

Alloy 353 MA development by Avesta took an alloy with similar nickel content (30-35%) as an RA330® alloy[(2)] (UNS N08330) or an alloy 800H (UNS N08010) which through microalloying could offer properties rivaling nickel alloys such as alloys 600 (UNS N06600) and 601 (UNS N06601). Table 1 shows a comparison of chemistries between S35315 and the other grades listed. Like alloy S30815, dramatic improvements in high temperature properties result from microalloying with cerium (oxidation, creep strength), silicon (oxidation), slightly higher carbon (creep strength), and significantly higher nitrogen (creep strength).

Alloy 602CA[(3)] is a nickel based alloy that has been developed by ThyssenKrupp VDM of Germany. The goal in the development of this alloy was to offer a material that extends the operating range of established nickel grades such as alloy 600 or 601 without the use of elements such as tungsten, molybdenum, or cobalt. These elements are commonly added to nickel superalloys, such as alloys X and 617 to enhance creep rupture properties, however, they also greatly increase the cost of the alloy and negatively impact oxidation resistance at more extreme temperatures. The yttrium addition in N06025 serves a similar purpose as the cerium addition in the "MA" alloys. Increased levels of aluminum also enhance oxidation resistance. An elevated carbon content coupled with additions of zirconium and titanium further improves creep rupture properties.

## ENVIRONMENTAL RESISTANCE

### Oxidation

As temperatures increase so does the rate of scaling from oxidation. Heat resisting alloys rely on the formation of a thin tightly adherent oxide scale. This layer acts as a barrier, which dramatically reduces the susceptibility of the alloy to further corrosion in the form of scaling. Chromium is the element most commonly employed to impart scaling resistance. In sufficient quantities (> 12%), chromium will react to form a continuous chromium oxide layer on the alloy surface. Typical chromium contents in wrought heat resistant alloys range from 15-25%. In recent decades, alloying with additional "rare earth" elements in small quantities or microalloying, has enhanced the stability of this chromium oxide scale[1]. Cerium, yytrium, and lanthanum are the more commonly used elements. Such alloying additions are becoming more common and are present in recent alloy developments such as S30815, S35315, N06025, as well as many others. Aluminum and silicon additions improve scaling resistance by forming continuous alumina and silica sublayers below the chromium oxide scale. These sublayers provide additional levels of protection between the atmosphere and the alloy.

3000 hour laboratory testing of alloys 253MA, 353MA, and 602CA along with several other commercially available heat resistant alloys was performed to compare their resistance to oxidation. Cyclic testing was performed in an electrically heated box furnace using ¼" (6.35mm) plate samples.

Samples measuring approximately ¼ x 3/4 x 2 inch (6.35mm x 19mm x 51mm) were prepared by grinding off all surfaces to remove areas affected by cutting operations and to remove mill surfaces. All

(2) RA330 is a registered trademark of Rolled Alloys
(3) 602CA is a registered trademark of Thyssen KruppVDM Technologies

samples were finish ground with 600 grit paper. Samples were cycled from the test temperature to room temperature weekly, all scale was collected in ceramic crucibles. In order to compensate for thermal gradients within the electrically heated box furnace the test tray was reversed after each cycle. In order to ensure retention of all scale, the specimens were covered immediately upon removal from the test furnace. The samples were weighed and a weight gain/unit area was calculated using the original surface areas of the specimens. Results of these tests are shown in Table 2.

Based on published data and field experience, a scaling rate less than 25 $mg/cm^2$ would indicated excellent resistance to scaling, 25 to 50 mg/cm would indicate usable resistance. If the scaling rate is greater than 50 $mg/cm^2$ then the alloy would not be suggested.

As the test series show the cerium containing S30815 had lower weight gains than types 309 stainless and alloy 800H even though it contains a lesser amount of nickel and chromium. The higher cerium and silicon levels allow this 11% nickel alloy to be utilized at temperatures through 2000°F, which is also the accepted temperature limit for 310 stainless.

The cerium containing alloy S35315 exhibited lower weight gains than other similar medium nickel alloys N08330 and N08810. It was also found that the S35315 exhibited lower weight gains than some nickel based alloys including alloy 600 and alloy X.

The yttrium containing alloy N06025 exhibited lower weight gains than all of the materials exposed in the test series. N06025 was the only alloy tested that was found to have an acceptable level of weight gain at 2200°F.

## CREEP-RUPTURE PROPERTIES

Metals behave differently at high temperatures than they do near room temperature. Loading of a metal bar to just below its yield strength at room temperature will not lead to failure or deformation regardless of the amount of time the stress is applied. At temperatures above 1000°F (538°C) and higher, mechanical strength is no longer independent of time. A metal component stressed to just below its yield point at red heat, for example 1500°F (816°C), will creep (stretch) slowly over time. Depending on the alloy, the stress level, and the temperature involved, the component could last for hours, weeks, or years until the metal finally fractures or ruptures. Because of creep, an alloy component can deform even under the stresses imposed by supporting its own weight. For this reason, the creep rupture strength is an important design criteria for any alloy intended for use above 1000°F (538°C).

The stable austenite matrix, solid solution strengthened by nitrogen and carbon, has resulted in a high creep deformation and rupture strength for the S30815 and S35315 alloys. Intragranular, and to some extent intergranular, carbide and nitride precipitation also contributes to this high strength. Any effect of the cerium addition on the creep properties is probably indirect, i.e. by reducing the amount and modifying the morphology of harmful intermetallic inclusions. It can be noted that above 1800°F (982°C) there are few other common grades that can compete in strength. A comparison of 10,000 hour creep-rupture strengths of several commonly used heat resistant grades is provided in Table 3.

The creep rupture properties of heat resisting alloys are heavily dependent on alloying content and grain size. In the case of N06025, its high creep-rupture strength is primarily a result of alloy content[5]. The relatively high carbon level ensures the precipitation of bulky homogeneously distributed carbides. Additions of titanium and zirconium ensure that these carbides and also carbonitrides are finely dispersed.

Even solution annealing at 2228°F (1220°C) does not dissolve the carbides completely. Thus, the alloy achieves its high creep rupture properties from a combination of solid solution hardening and carbide strengthening. The result is an alloy with greater creep-rupture properties than traditional alloys such as N08330 and alloy 601. Further comparison indicates that at extreme temperatures N06025 compares favorably to other heat resistant nickel alloys.

Due to the excellent creep properties of the N06025 and S30815, ASME has approved both for Section VIII, Division 1 applications. S30815 is permitted for use up to 1650°F (899°C) and UNS N06025 is one of the few materials permitted for use to 1800°F (982°C), ASME Code Case 2359

## APPLICATIONS

In the manufacture of foam glass for insulation the mixture of glass and foaming agent are contained and added to an alloy "baking pan". These are shown in figure 1. The pan is essentially a mold for the glass as it expands, while passing through a furnace between 1600-1700°F (871-927°C). Stainless steels such as 309 and 310 had been used prior to the development of S30815. The repeated cycling leads to distortion of the pans. Eventually distortion requires restraightening or replacement of the alloy pans. As a result of its elevated creep rupture properties, S30815 became the standard material of construction.

Anti-vibration devices often called wrinkle or handcuff bars are being manufactured using UNS S35315. The manufacturer has switched from UNS S30815 and the nickel alloy UNS N08330. In this application, 3/16 inch (4.76 mm) plate strips are corrugated, so that two bars when welded together, wrap around a span of several superheater tubes. These assemblies reduce tube vibration. UNS S35315 heavy plate has also been used for header supports. To date, UNS S35315 alloy has been utilized in direct-fired boilers, heat recovery steam generators (HRSGs), and waste incinerator boilers. Figure 2 shows examples of how UNS S35315 is used. Temperatures depending on the boiler type can reach approximately 2000°F (1093°C).

The improved scaling resistance of N06025 has led to its selection to replace alloy 601 in a stainless steel sintering operation, figure 3. The user manufactures stainless steel orthodontic appliances via the sintering process. In order to sinter the stainless powders together, external temperatures of the retort can be as high as 2300°F (1260°C). Excessive scaling is the limiting factor determining retort life. Sheets 1/8 inch (3.2 mm) thick of N06025 alloy are being used to fabricate the replacement retort body.

Bellybands used as reinforcement on the exterior of an alloy 600 retort were used as a field test program for N06025. Historically, alloy 600 has been used for the retort and any external reinforcements. The externally heated retort is used for a process that coats turbine blades with an aluminide coating. Temperatures on the outside of the retort can reach temperatures estimated at 2100°F (1149°C). After more than 12 months in this cyclic service the N06025 belly band remained straight and showed negligible oxidation. The alloy 600 bellybands, in contrast display significant warping and have thinned due to oxidation. The user of these retorts standardized on N06025 for subsequent retorts for two reasons. Reduced warpage will improve the longevity of the retorts between repairs. Equally important the significantly reduced scaling will reduce contamination of the turbine blades being manufactured. This will reduce expenses related to part rejections. N06025 has also replaced alloy 600 for the internal coating cans, which contain the blades during high temperature processing.

## CONCLUSIONS

Application of microalloying techniques to stainless steels have extended the range of applications for this family of alloys. Cerium and nitrogen additions allow microalloys, such as S30815 and S35315 to achieve strength levels double that of traditional 300 series stainless steels. As a result, many applications that in the past may have required nickel-based alloys now have an option of being served by leaner nickel grades. The use of these lower nickel grades can as a result reduce the life cycle costs of high temperature components. The application of microalloying techniques to nickel based alloys such as N06025 extend the maximum operating range for nickel alloys to beyond 2200°F (1204°C).

## REFERENCES


1. M. Willfor, P. Vangeli -AvestaPolarit 353 MA® - A Problem Solver for the Steel and Metals Industry. AISE/2003

## TABLE 1

## NOMINAL COMPOSITION OF HIGH TEMPERATURE ALLOYS (WEIGHT %)

| Alloy | UNS | Ni | Cr | Si | Al | Fe | C | N | Ce/Y | Other |
|---|---|---|---|---|---|---|---|---|---|---|
| **353MA** | **S35315** | **35** | **25** | **1.2** | **-** | **36** | **0.05** | **0.16** | **0.05 Ce** | |
| **253MA** | **S30815** | **11** | **21** | **1.7** | **-** | **65** | **0.08** | **0.17** | **0.04 Ce** | |
| **602CA** | **N06025** | **63** | **25** | **-** | **2.2** | **9.5** | **0.2** | **-** | **0.10 Y** | **Ti, Zr,** |
| **309 SS** | **S30908** | **13** | **23** | **0.8** | **-** | **62** | **0.05** | **-** | **-** | |
| 310 SS | S31008 | 20 | 25 | 0.5 | - | 52 | 0.06 | - | - | |
| 800H | N08810 | 31 | 21 | 0.4 | 0.4 | 45 | 0.06 | - | - | Al, Ti |
| Alloy 330 | N08330 | 35 | 19 | 1.25 | - | 43 | 0.05 | - | - | |
| Alloy 600 | N06600 | 76 | 15.5 | 0.2 | 0.2 | 8 | 0.05 | - | - | Ti |
| Alloy 601 | N06601 | 61.5 | 22.5 | 0.2 | 1.4 | 14 | 0.05 | - | - | |
| Alloy 617 | N06617 | 54 | 22 | 0.03 | 1 | 1.5 | 0.08 | - | - | 9Mo,12.5Co,Ti |
| Alloy X | N06602 | 47 | 22 | 0.3 | - | 19 | 0.08 | - | - | 9Mo, 1.7Co, W |

## TABLE 2

## CYCLIC OXIDATION TESTING IN AIR
## 3000 HOURS – 168 HOUR CYCLES
## WEIGHT CHANGE ($mg/cm^2$)

| Alloy | 1800°F | 2000°F | 2100°F | 2200°F |
|---|---|---|---|---|
| **UNS S35315** | **4.4** | **21** | **36** | **232** |
| **UNS S30815** | **8.7*** | **41** | **110** | **-** |
| UNS S30908 | 16.2 | 104* | - | - |
| UNS S31008 | 5.2 | -- | 80 | - |
| UNS N08330 | 4.2 | 32 | 54 | - |
| UNS N08810 | 32.0 | 143 | 295 | - |
| **UNS N06025** | **-** | **11** | **18** | **48** |
| UNS N06617 | - | - | 30 | ** |
| UNS N06600 | - | - | 74 | 453 |
| UNS N06601 | - | 13 | 22 | 114 |
| UNS N06602 | - | - | 58 | - |

* Test run for 1966 hours

** N06617 removed from testing after one cycle due to excessive scaling

## TABLE 3

## AVERAGE 10,000 HOUR STRESS TO RUPTURE STRENGTH, psi

| ALLOY | 1200°F | 1400°F | 1600°F | 1800°F | 2000°F | 2100°F | 2200°F |
|---|---|---|---|---|---|---|---|
| **UNS S35315** | **12,200** | **5,400** | **2,600** | **1,300** | **680** | **(450)** | **(320)** |
| **UNS S30815** | **14,000** | **5,200** | **2,500** | **1,150** | **680** | **--** | **--** |
| **UNS N06025** | **31,200** | **11,300** | **3,200** | **1,490** | **670** | **440** | **290** |
| UNS S31008 | 14,400 | 4,500 | 1,500 | 660 | -- | -- | -- |
| UNS N08330 | 11,000 | 4,300 | 1,700 | 630 | (280) | -- | -- |
| UNS N08810 | 17,500 | 7,300 | 3,500 | 1,200 | -- | -- | -- |
| UNS N06601 | 22,000 | 7,000 | 1,850 | 820 | (330) | (200) | |
| UNS N06600 | 13,500 | 6,200 | 2,350 | 1,150 | | | |
| *UNS N06617* | *45,000* | *13,000* | *5,000* | *2,000* | *700* | | |

*UNS N06617 data interpreted from graphical data*

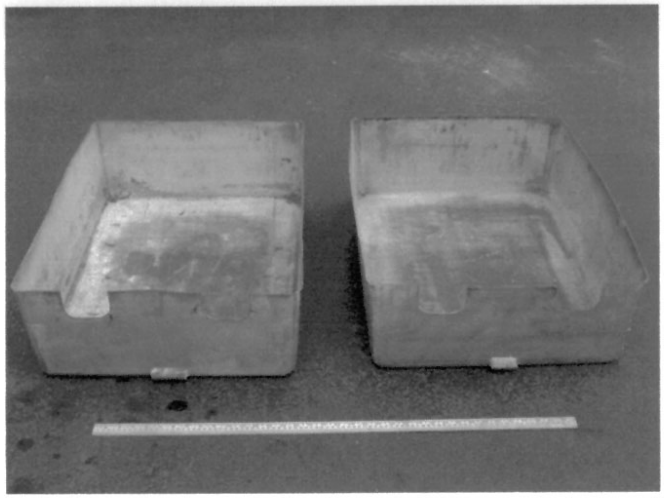

Figure 1 - Alloy 253 MA pans used in the production of foam glass insulation. Baking of the foam glass occurs at 1600-1700°F. S30815 sheet is the standard material over 309 and 310 stainless.

Figure 2 – Photo showing UNS S35315 anti-vibration straps used in an auxiliary steam boiler. This unit was installed at a natural gas fired co-generation plant. UNS S35315 replaced UNS S30815 and UNS N08330 as the material of choice. UNS S35315 has been used for over 4 years by this boiler OEM.

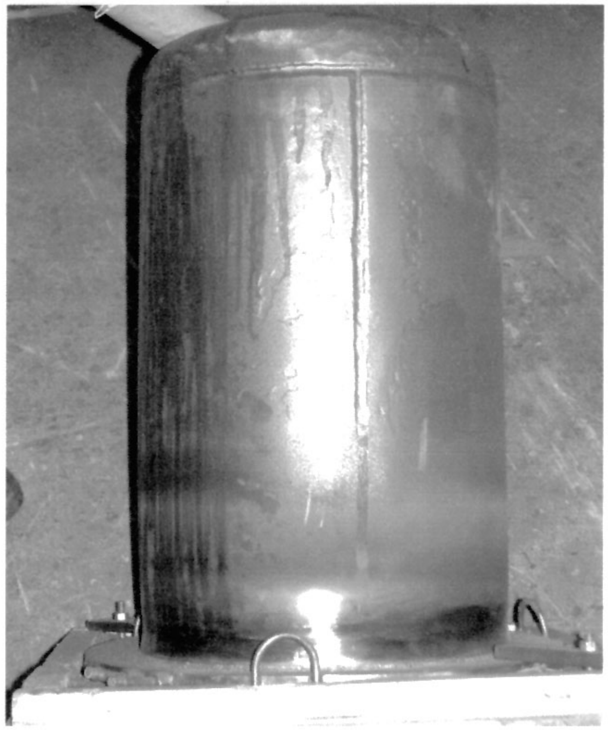

Figure 3 – N06601 retort used for sintering stainless steel orthodontic appliances. Operating temperatures exceed 2200°F (1204°C) with hydrogen gas on the interior of the retort. 11ga UNS N06025 has been used for the replacement retort. Scaling of the retorts external surface and excessive oxidation of the alloy 82 welds are evident.

Figure 4 – Photo showing test belly bands of alloy 600 first and third from left compared to bands fabricated from UNS N06025 (2nd and 4th from left) using ¼" (6.35 mm) plate. This retort was operated for over 12 months in cyclical service. The external surface of this coating retort sees air at approximately 2100°F (1149°C).